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(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Styrene Oxide Products

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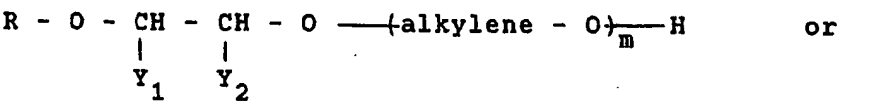
(57) 18 Claims

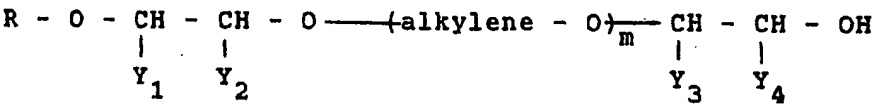
Styrene oxide products

Abstract

Styrene oxide products of the formula

(1) 

or

(2) 

where R is an aliphatic radical having 1 to 24 carbon atoms, "alkylene" is an alkylene radical of 2 or 3 carbon atoms, one of Y_1 and Y_2 is phenyl and the other is hydrogen, m is a number from 1 to 100, and one of Y_3 and Y_4 is phenyl and the other is hydrogen, their acid esters and salts thereof. These products are a novel class of nonionic or anionic surfactants which are useful as textile processing aids, in particular as emulsifiers, dyeing assistants, wetting agents, deaerating agents or padding assistants.

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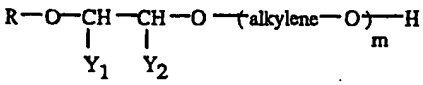
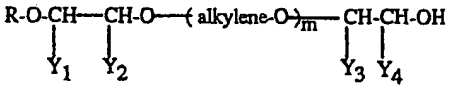
Styrene oxide products

The present invention relates to novel styrene oxide products and the use thereof as textile processing aids, in particular as emulsifiers, dyeing assistants and especially as wetting agents or padding assistants.

The styrene oxide products according to the present invention conform to the formula

(1)  or the formula

(2) 

and are also prepared in the form of their acid esters and salts thereof.

In the formulae (1) and (2), R is an aliphatic radical having 1 to 24 carbon atoms.

"alkylene" is an alkylene radical of 2 or 3 carbon atoms such as ethylene or propylene or a combination thereof. m is a number from 1 to 100, preferably from 2 to 50.

Of the substituent pairs (Y_1 and Y_2) and (Y_3 and Y_4), one Y is phenyl and the other Y is hydrogen.

The substituent R is advantageously the hydrocarbon radical of a saturated or unsaturated aliphatic monoalcohol having 1 to 24 carbon atoms. The hydrocarbon radicals can be straight-chain or branched. Preferably, R is an alkyl or alkenyl radical having 4 to 22 carbon atoms.

Suitable aliphatic saturated monoalcohols are for example methanol, ethanol, propanol, isopropanol, butanols, pentanols, hexanols, heptanols, octanols, nonanols, decanols, lauryl

alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, arachidyl alcohol or behenyl alcohol, and also oxo process alcohols such as, in particular, 2-ethylbutanol, 2-methylpentanol, 5-methylheptan-3-ol, 2-ethylhexanol, 1,1,3,3-tetramethylbutanol, 2-octanol, isononyl alcohol, trimethylhexanol, trimethylnonyl alcohol, C_9-C_{11}oxoalcohol, tridecyl alcohol, isotridecanol or linear primary alcohols (Alfols) having 8 to 18 carbon atoms. Some Alfol representatives are Alfol (8-10), Alfol (9-11), Alfol (10-14), Alfol (12-13) or Alfol (16-18). ("Alfol" is a registered trade mark).

Unsaturated aliphatic monoalcohols are for example vinyl alcohol, allyl alcohol, dodecenyl alcohol, hexadecenyl alcohol and oleyl alcohol.

The alcohol radicals can be present singly or in the form of mixtures of two or more components, such as mixtures of alkyl and/or alkenyl groups derived from soyabean fatty acids, palm kernel oil fatty acids or tallow oils.

$(Alkylene\text{-}O)_m$- chains are preferably of the ethylene glycol, propylene-ethylene glycol or ethylene-propylene glycol type; the first is particularly preferred.

m is preferably 2 to 25.

The styrene oxide products of the formula (1) are prepared by first etherifying the aliphatic monoalcohol with 1 mole of the styrene oxide and then by the addition of 1 to 100 moles of an alkylene oxide (ethylene oxide and/or propylene oxide) to the resulting R-O-substituted phenylethanol.

The styrene oxide products of the formula (2) are prepared by etherifying the products of the formula (1) terminally with a further mole of styrene oxide.

The etherification of monoalcohol with styrene oxide and also the terminal addition of styrene oxide to prepare the products of the formula (2) is advantageously carried out in a virtually anhydrous or substantially anhydrous medium at a temperature of 40 to 90°C under atmospheric or super atmospheric pressure and in the presence of an acidic catalyst, e.g. BF_3 etherate, p-toluenesulfonic acid, or in particular concentrated sulfuric acid (90-98 %). The acid is then removed by neutralizing and filtering.

The addition of the alkylene oxide to the substituted phenylethanol is carried out in a

conventional manner using ethylene oxide or propylene oxide or alternately ethylene oxide and propylene oxide or a mixture of ethylene oxide and propylene oxide.

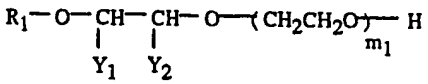
The acid esters can be present, depending on the acid radical, in the form of monoesters, diesters or half esters and as free acids or preferably as salts, for example alkali metal salts or alkaline earth metal salts or ammonium salts. Suitable alkali metal salts are in particular the sodium, potassium and lithium salts, suitable alkaline earth metal salts are magnesium and calcium salts, and suitable ammonium salts are the ammonium, dimethylammonium, trimethylammonium, monoethanolammonium, diethanolammonium and triethanolammonium salts. Preferably, the acid esters are prepared as ammonium salts. Mono- or diethanolammonium salts may additionally be etherified with 1 to 4 oxyethylene units.

The acid esters are prepared by reacting the nonionic styrene oxide product of the formula (1) or (2) according to the present invention with an at least dibasic oxygen acid and if desired converting the resulting acid ester into the abovementioned salts.

Suitable polybasic oxygen acids for forming the acid esters are sulfonated or sulfonyl-free, organic, preferably aliphatic, dicarboxylic acids of 3 to 6 carbon atoms, e.g. maleic acid, malonic acid, succinic acid or sulfosuccinic acid, and polybasic inorganic oxygen acids, e.g. sulfuric acid or orthophosphoric acid. In place of the acids it is also possible to use their functional derivatives such as anhydrides, halides or amides. Examples of these functional derivatives are maleic anhydride, phosphorus pentoxide, chlorosulfonic acid and sulfamic acid. The phosphoric esters are advantageously formed as mixtures of a monoester and diester.

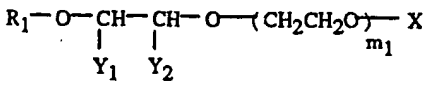
The esterification is in general carried out by simply mixing the reactants and heating, advantageously to a temperature between 50° and 100°C. The free acids which are initially formed can subsequently be converted into the corresponding alkali metal or ammonium salts. The conversion into the salts is carried out in a conventional manner by adding bases, for example ammonia, monoethanolamine, triethanolamine or an alkali metal hydroxide, for example sodium hydroxide or potassium hydroxide. In a particularly preferred embodiment, sulfuric acid esters are directly prepared in the form of their ammonium salts by heating the nonionic styrene oxide products with sulfamic acid in the presence or absence of urea.

Industrially important styrene oxide products conform to the formula

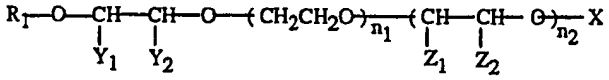
(3) 

where R_1 is alkyl or alkenyl each having 1 to 22 carbon atoms, preferably 4 to 22 carbon atoms, one of Y_1 and Y_2 is phenyl and the other is hydrogen, and m_1 is from 2 to 40.

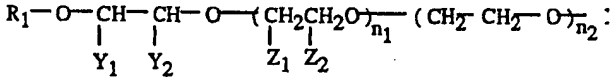
Preferred acid esters prepared with an inorganic or organic acid conform to the formula

(4) 

or the formula

(5) 

or the formula

(6) 

where R_1, Y_1, Y_2 and m_1 are each as defined, one of Z_1 and Z_2 is methyl and the other is hydrogen, X is the maleic acid, sulfosuccinic acid, sulfuric acid or phosphoric acid radical, and the sum $n_1 + n_2$ is from 2 to 30, preferably from 4 to 18.

Preferred acid esters of the formulae (4), (5) and (6) contain either a maleic ester group or a sulfuric acid ester group, which are each preferably present in the form of the alkali metal salts or ammonium salts.

Of particular interest are the acid phosphoric esters of the addition products of the formula (3) in which the phosphoric acid esters are advantageously present as mixtures of the corresponding salts of a mono- and diester.

If desired, the styrene oxide products of the formula (3) may be terminally etherified with a further mole of styrene oxide and if necessary then converted with an at least dibasic oxygen acid into the acid ester and into the corresponding salt. Both the terminal styrene oxide addition and the subsequent esterification can be carried out under the above-mentioned conditions.

Styrene oxide products according to the present invention are suitable for a wide range of uses in textile application, such as pretreatment, dyeing or finishing. Nonionic unesterified products are useful in particular as assistants in the dyeing of polyamide-containing fibre materials with anionic dyes or dye mixtures. The corresponding acid esters, in particular dicarboxylic monoesters or acid esters of sulfuric acid and primarily phosphoric esters, by contrast, are used in particular as wetting agents, deaerating agents and foam suppressants in aqueous systems, in particular in the dyeing of natural or synthetic fibre material, primarily in the dyeing of cellulose textile materials, polyester fibres or natural or synthetic polyamide fibre materials. Both as nonionic products and as acid esters, the styrene oxide products according to the present invention improve, if formulated as described, the affinity of the dyes and thereby speed up the diffusion of the dyes into the fibres.

The present invention accordingly also provides a method for processing (finishing) natural or synthetic fibre material in the presence or absence of appropriate dyes, which comprises processing in the presence of the nonionic and/or anionic styrene oxide products according to the present invention.

The amounts in which the styrene oxide products according to the present invention are added to the processing liquors, such as dyeing liquors or pretreatment or aftertreatment liquors, vary with the substrate, advantageously between 0.5 and 20 g, preferably between 1 and 10 g, per litre of liquor.

Advantageous formulations of the styrene oxide products according to the present invention contain them as nonionic and/or anionic compounds with or without water in combination with nonionic or anionic dispersants, fatty alcohols, fatty acid amides, alkylene bis fatty acid amides, alkyl alkenyldicarboxylates, metal stearates, silicone oils, e.g. -dialkylpolysiloxanes, or even mineral oils or alkanolamines in stable, wetting and/or defoaming preparations. Such preparations are also capable of virtually completely deaerating aqueous systems. It is thus possible to avoid air inclusions not only in the

application baths but also in the substrates. Such deaeration makes it possible to avoid spotting in dyeing and finishing.

Preference is given to aqueous or water-free preparations which, based on the preparation as a whole, comprise

(A) 2 to 50 % by weight of an acid ester of the styrene oxide product of the formula (1) or (2),

(B) 5 to 50 % by weight of a nonionic surfactant, preferably an aliphatic monoalcohol having 6 to 22 carbon atoms or the product of the addition of 2 to 80 moles of ethylene oxide to 1 mole of an aliphatic monoalcohol having 6 to 22 carbon atoms or a polyoxyethylene derivative of a sorbitan fatty acid ester or of a styrene oxide product of the formula (1) or (2) or mixtures thereof and at least one of the following components:

(C) 1 to 30 % by weight of a silicone oil, for example a dialkylpolysiloxane such as dimethylpolysiloxane,

A (D) 10 to 60 % by weight of a mineral oil, for example a paraffin oil such as Shell* oil L 6189 or mineral oils Esso* 301 to 312,

(E) 20 to 45 % by weight of a dialkyl ester of an ethylenically unsaturated aliphatic dicarboxylic acid, preferably containing 4 to 12 carbon atoms per each alkyl moiety, e.g. bis-2-ethylhexyl maleate or bis-2-ethylhexyl citraconate,

(F) 10 to 70 % by weight of a diffusion accelerant, in particular an aliphatic or aromatic carboxylic ester such as C_4-C_{12}alkyl lactate, C_4-C_{12}alkyl benzoate, phenyl benzoate or benzyl benzoate, or else an alkylbenzene, such as trimethylbenzene or ethylbenzene,

(G) 0.5 to 5 % by weight of a salt of a C_{10}-C_{24}fatty acid and a polyvalent metal, e.g. magnesium distearate, calcium dibehenate or aluminium tristearate, and

(H) 0.5 to 3 % by weight of a C_1-C_4alkylenediamide of a fatty acid having 10 to 24 carbon atoms, e.g. methylenebisstearamide, ethylenebisstearamide or ethylenebisbehenamide.

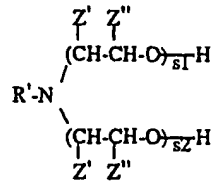
Further preferred aqueous preparations which are in particular used as assistants for

*Trade-mark

dyeing natural or synthetic polyamide fibres, especially wool, with anionic dyestuffs, comprise based on the preparation as a whole,

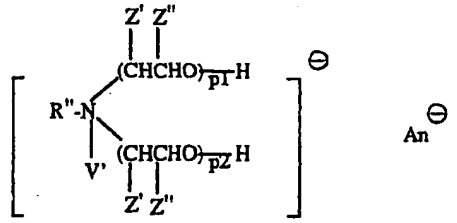
(a) 15 to 50 % by weight of a nonionic styrene oxide product of the formula (1) or (2), in particular a styrene oxide product of the formula (3),

(b) 1 to 5 % by weight of an acid ester or salt thereof, for example an alkali metal or ammonium salt, of a compound of the formula

(7) 

or of a quaternized product of the acid ester or salt thereof, where R' is alkyl or alkenyl having 12 to 22 carbon atoms, one of Z' and Z" is hydrogen, methyl or phenyl and the other is hydrogen and s_1 and s_2 are each integers such that their sum, $s_1 + s_2$, is from 2 to 100,

(c) 2 to 10 % by weight of a quaternary ammonium compound of the formula

(8) 

where R" is an alkyl or alkenyl radical having 12 to 22 carbon atoms, V' is a substituted or unsubstituted alkyl, such as methyl, ethyl, benzyl or $-CH_2CONH_2$, one of Z' and Z" is hydrogen, methyl or phenyl and the other is hydrogen, $An^{\ominus}$ is an anion of inorganic or organic acid, and p_1 and p_2 are each integers such that the sum of p_1 and p_2 is from 2 to 100, with or without one or more of the following components:

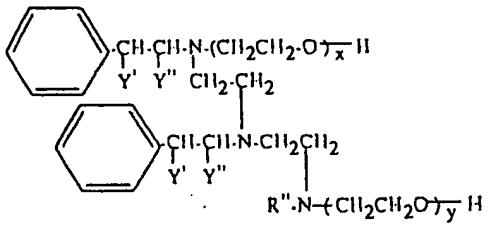
(d) 0.5 to 25 % by weight of a polyalkylene glycol ether of the formula

(9) 

where R''' is an alkyl or alkenyl radical having 4 to 22 carbon atoms, "alkylene" is

ethylene or propylene, and q is from 2 to 85, and

(e) 0.5 to 5% by weight of a nitrogen-containing nonionic compound of the formula

(10) 

wherein R" is an alkyl or alkenyl radical having 12 to 22 carbon atoms, one of Y' and Y" is phenyl and the other is hydrogen, and x and y are each integers such that the sum of x and y is from 80 to 140.

Further details and preferred combinations and use forms of components (b), (c), (d) and (e) may be found in DE-A-1,568,258, publication date April 9th, 1970, DE-A-1,619,385, publication date June 9th, 1971, EP-A-89004, publication date September 21st, 1983 and EP-A-312493, publication date April 19th, 1989.

In the preparation and use examples below, percentages and parts are by weight, unless otherwise stated. The dye quantities are based on commercial, i.e. extended material, and the auxiliary quantities are based on pure substance.

Preparation examples

Example 1: a) 540 g of 3,5,5-trimethylhexanol are heated to 80°C together with 15 g of 96% sulfuric acid. 300 g of styrene oxide are added dropwise over 70 minutes, during which the temperature is maintained at between 80 and 90°C. The reaction mixture is

then stirred at 86°C for 5 hours, and thereafter stirred until cold, neutralized with sodium bicarbonate solution and filtered, and the aqueous phase is separated off. After the excess 3,5,5-trimethylhexanol has been distilled off, the residue is subjected to a fractional distillation under a high vacuum.

The result obtained is 304.6 g of a colourless product of formula

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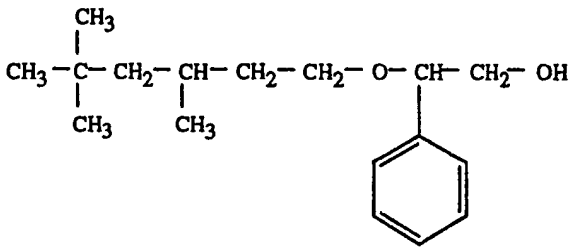
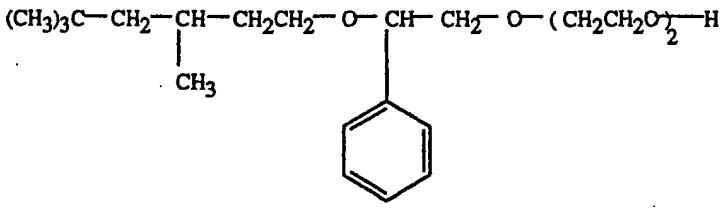
(11) 

b.p.: 105-106°C/10^{-2} OH number: 213

b) 263 g of 3,5,5-trimethylhexyloxyphenylethanol of the formula (11) are reacted in the presence of 1 % sodium methoxide with 88 g of ethylene oxide at 140°C and 8 bar pressure.

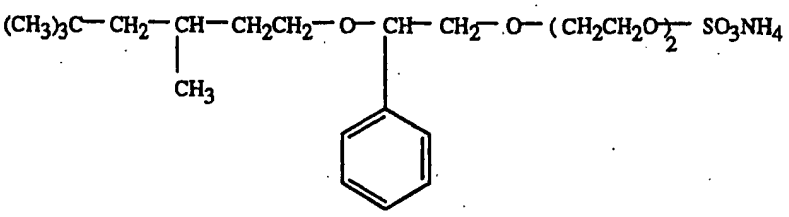
The result obtained is a product of the formula

(12) 

OH number: 156

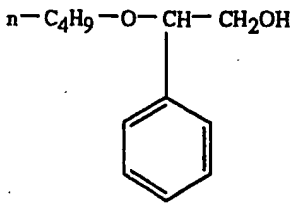
c) 70.2 g of the product of the formula (12) are heated to 60°C and stirred with 20.8 g of urea for 15 minutes. 20.8 g of sulfamic acid are then added, and the mixture is heated to 70°C, stirred at 70°C for 1 hour, heated to 95°C and stirred at 95°C for a further 2 hours.

Addition of 111.8 g of water gives a viscous, gellike solution of the product of the formula

(13) 

Example 2: a) 333 g of n-butanol are heated to 65°C together with 13.4 g of 96 % sulfuric

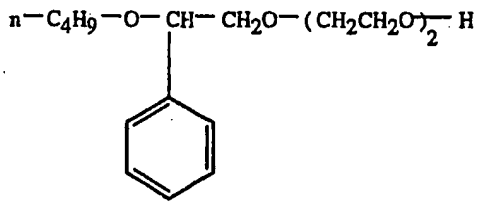
acid. 345.6 g of styrene oxide are added dropwise over 30 minutes during which the temperature rises to 108°C. The reaction mixture is subsequently stirred at 75°C for 2 hours, then stirred until cold and neutralized with sodium bicarbonate solution, and filtered. The excess butanol is distilled off, and the product is subjected to a fractional distillation under a high vacuum. The result obtained is 201 g of n-butyloxyphenylethanol of the formula

(14) 

b.p.: 96-100°C/10^{-2} OH number: 286

b) 192 g of n-butyloxyphenylethanol are reacted in the presence of 1 % of sodium methoxide with 81.8 g of ethylene oxide at 140°C and 6 bar pressure.

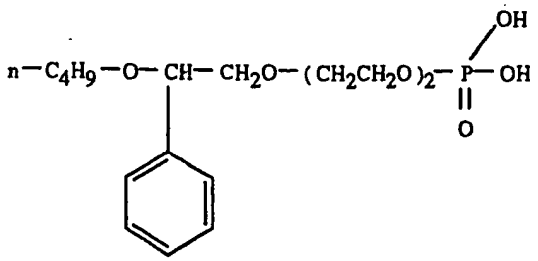
The result obtained is a product of the formula

(15) 

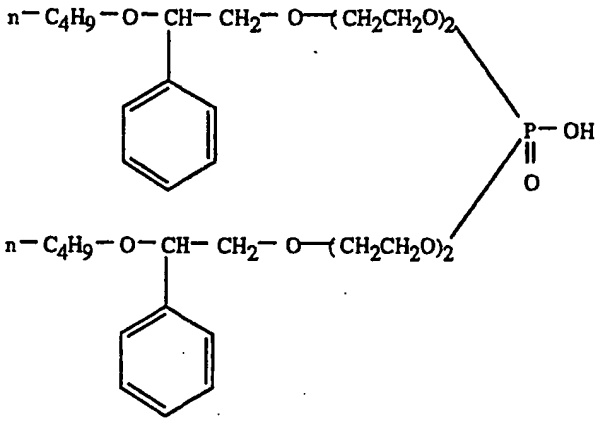
OH number: 199

c) 56.3 g of the adduct of the formula (15) are reacted with 9.5 g of phosphorus pentoxide at room temperature with rapid stirring. In the course of the reaction, the temperature rises to 65°C. The mixture is subsequently stirred at room temperature for 4 hours, producing a mixture of monophosphoric and diphosphoric esters of the formulae

(16a)



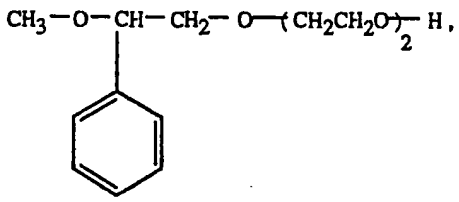
(16b)



The reaction product is clear and viscous.

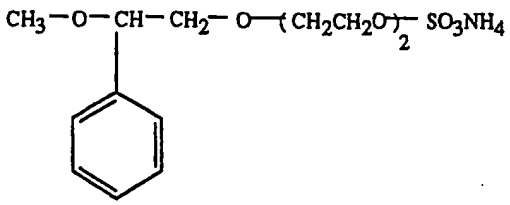
Example 3: 51 g of the adduct of the formula

(17)

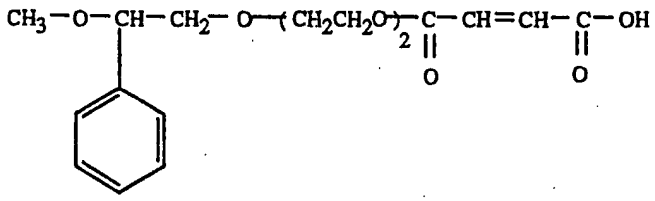


OH number:219

prepared as described in Example 1b), are heated to 60°C and stirred with 20.8 g of urea. 20.8 g of sulfamic acid are then added, and the mixture is heated to 70°C, stirred at 70°C for 1 hour, heated to 95°C and stirred at 95°C for a further 2 hours. Addition of 92.6 g of water gives a water-miscible, slightly viscose solution of the product of the formula

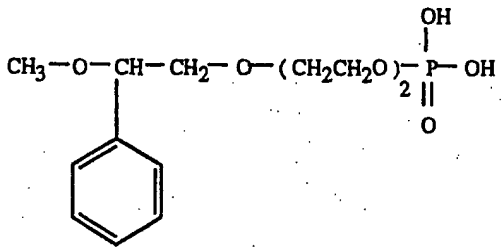
(18) 

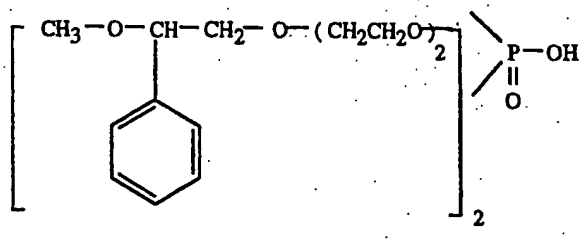
Example 4: 63.75 g of the adduct of the formula (17) are slowly heated to 70°C together with 24.5 g of maleic anhydride. The mixture is then stirred at 70°C for 1 hour, heated to 90°C and stirred at 90°C for a further 3 hours. The result obtained is a highly viscous product of the formula

(19) 

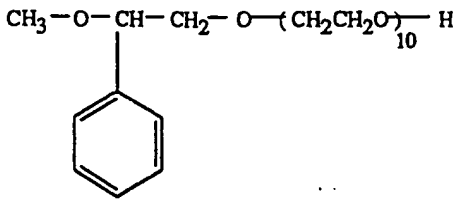
The acid number is 161.

Example 5: 11.35 g of phosphorus pentoxide are added with stirring at room temperature to 61.2 g of the adduct of the formula (17). In the course of addition, the temperature rises to 80°C. The mixture is subsequently stirred at room temperature for 4 hours, turning into a viscous mixture of phosphoric esters of the formulae

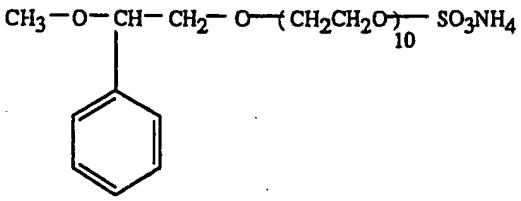
(20a) 

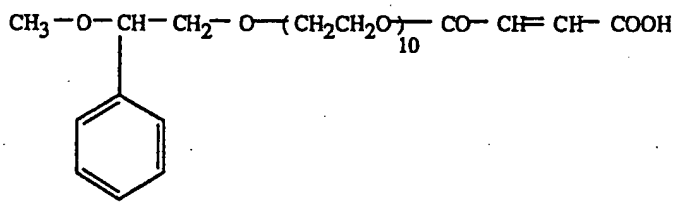
(20b) 

The procedure of Examples 1 to 5 is repeated using appropriate starting materials to obtain the following nonionic and anionic addition products:

(21) 

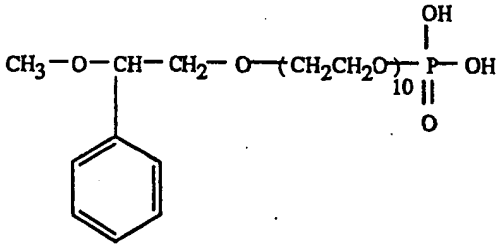
OH number:92

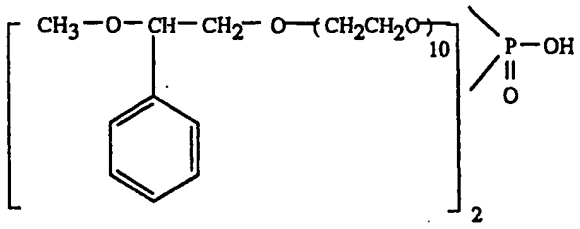
(22) 

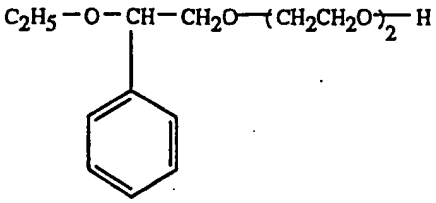
(23) 

Acid number: 78.8

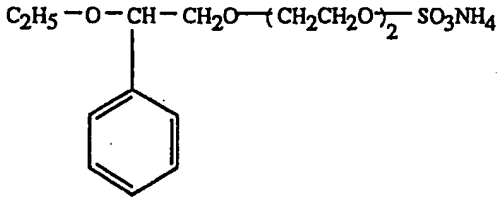
Mixture of a phosphoric monoester and diester of the formulae (24a) and (24b)

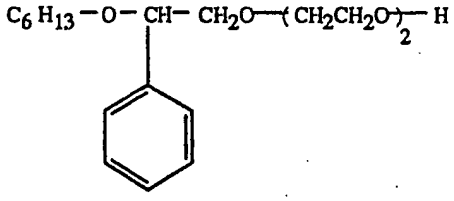
(24a) 

(24b) 

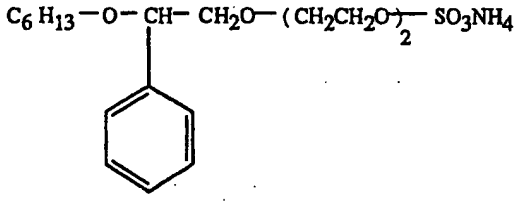
(25) 

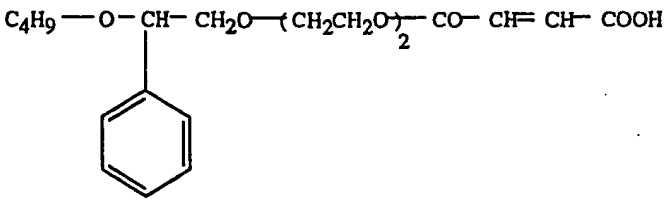
OH number: 223

(26) 

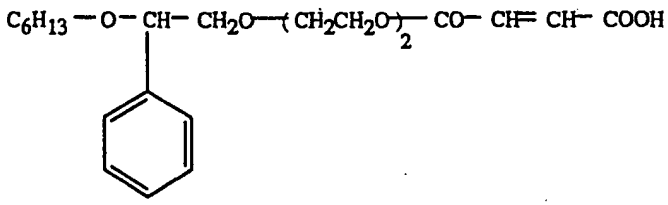
(27) 

OH number: 185

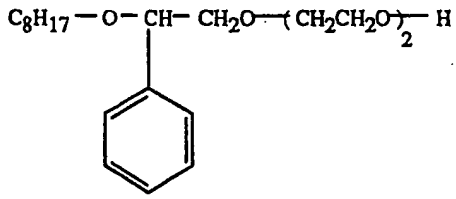
(28) 

(29) 

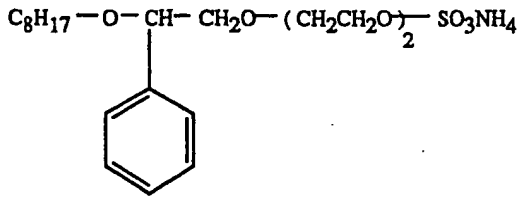
Acid number: 148.5

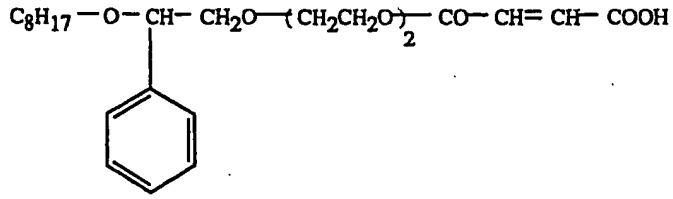
(30) 

Acid number: 145

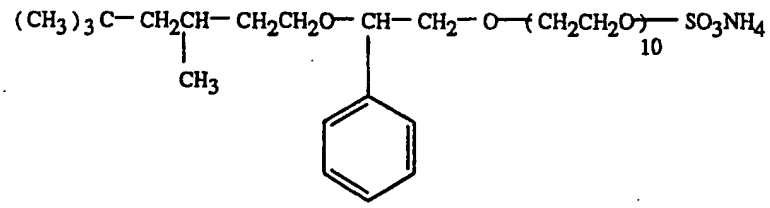
(31) 

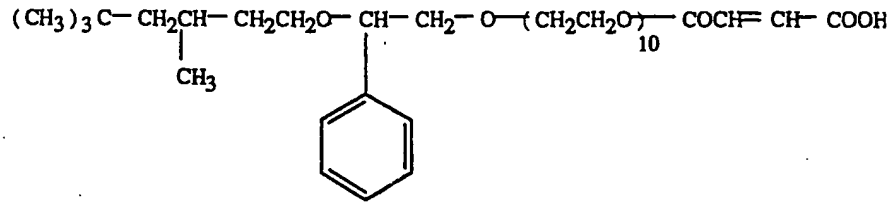
OH number: 156

(32) 

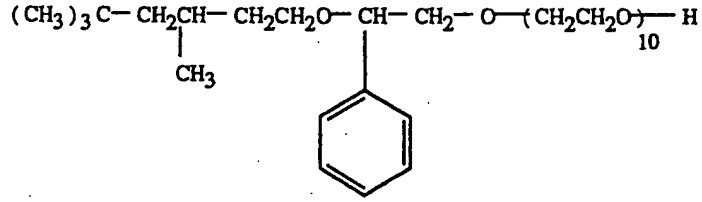
(33) 

Acid number: 127

(34) 

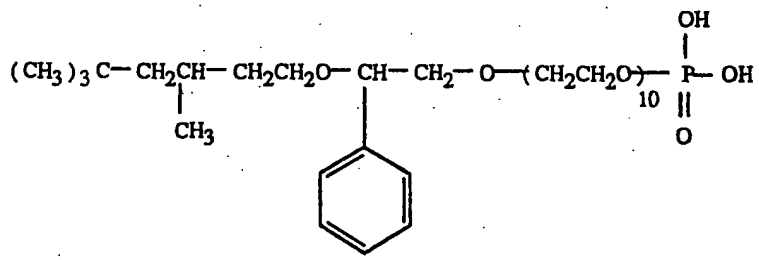
(35) 

Acid number: 98

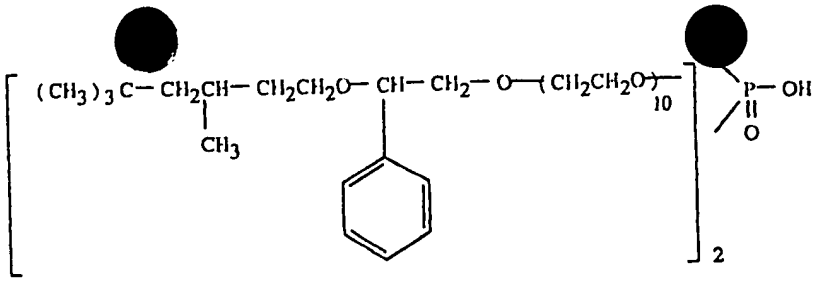
(36) 

OH number: 116

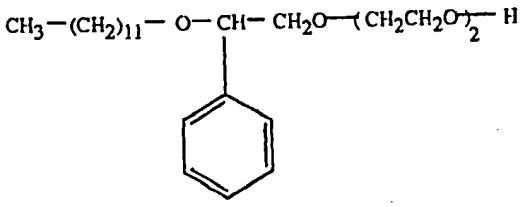
Mixture of a phosphoric monoester or diester of the formulae (37a) and (37b)

(37a) 

(37b)

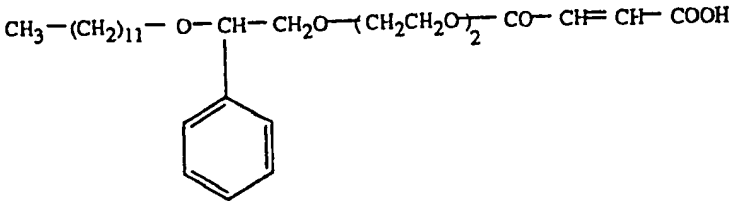


(38)



OH number: 154

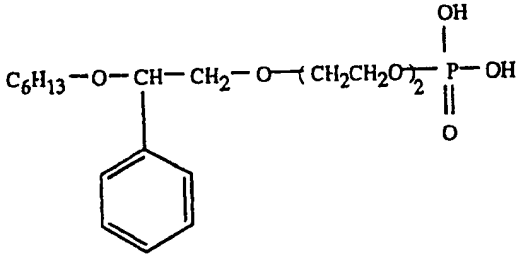
(39)



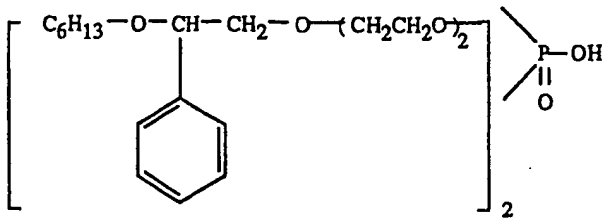
Acid number: 124

Mixture of a phosphoric monoester and diester of the formulae (40a) and (40b)

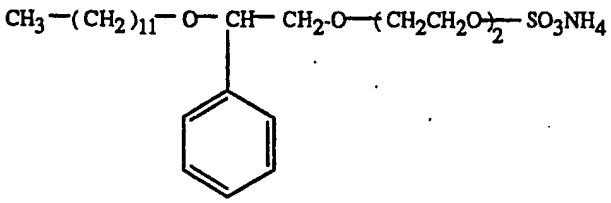
(40a)



(40b)

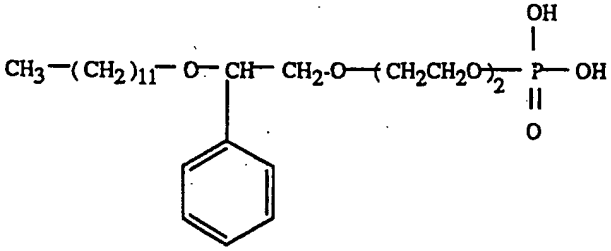


(41)

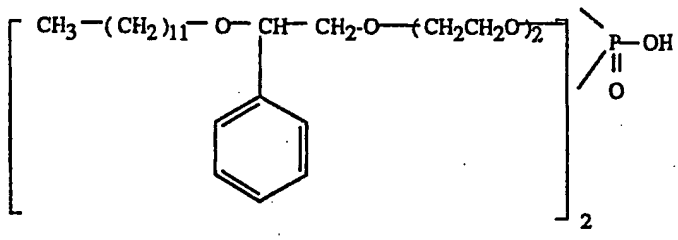


Mixture of a phosphoric monoester and diester of the formulae

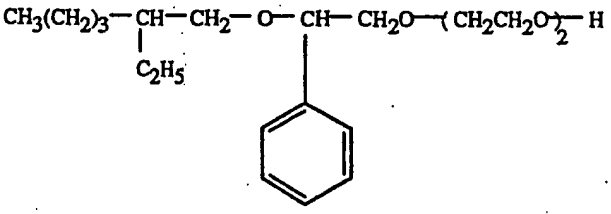
(42)



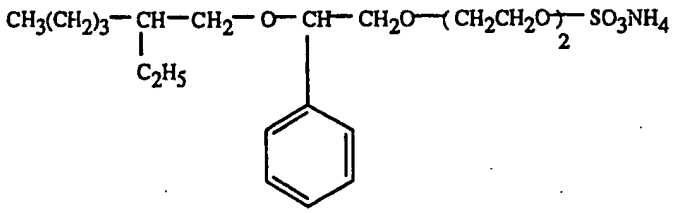
(43)

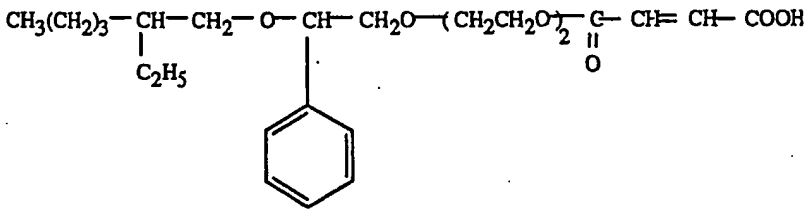


(44)



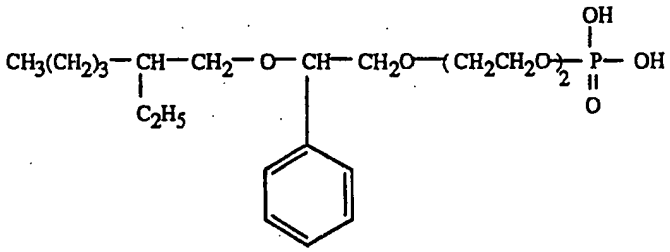
OH number: 177

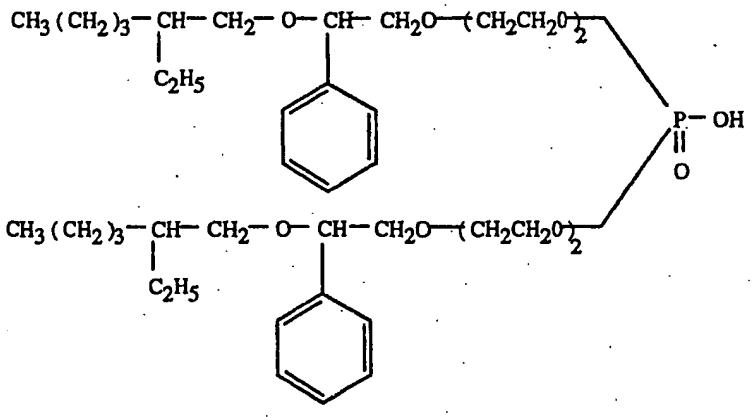
(45) 

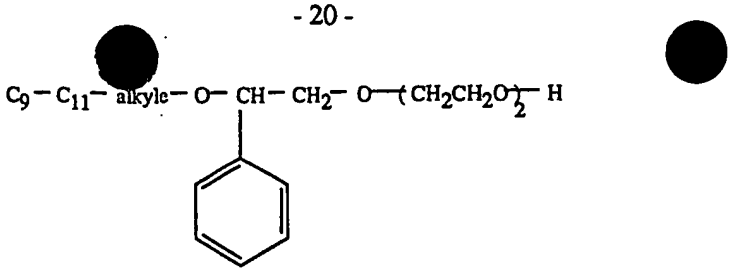
(46) 

Acid number: 140

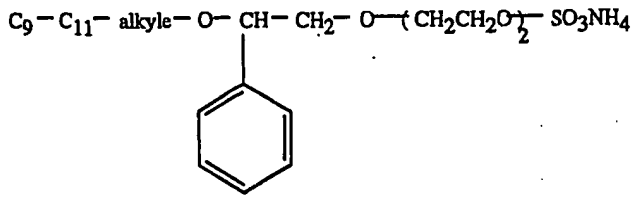
Mixture of a phosphoric monoester and diester of the formulae

(47a) 

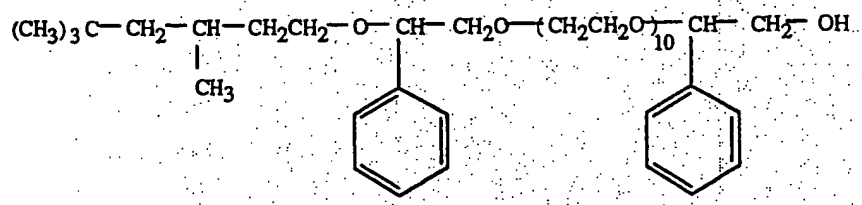
(47b) 

(48) 

OH number: 160

(49) 

Example 6: 120 g of the addition product of the formula (36) (OH number: 116) are admixed with 1.8 g of concentrated sulfuric acid (96 %), and the mixture is heated to 65°. 30 g of styrene oxide are then added dropwise over 30 minutes, during which the temperature rises to 82°C. The reaction product is then stirred at 75°C for 5 hours, neutralized with sodium bicarbonate solution and filtered. The filtrate is concentrated, and the residue is dried. The result obtained is a clear, yellow product of the formula

(50) 

OH number: 95

Use examples

Example 7: 100 g of wool serge are wetted out in a circulation machine at 40°C in the course of 15 minutes with a liquor comprising 1.1 litres of water and the following additives:

3.2 g of 80 % acetic acid
5.0 g of calcined sodium sulfate
1 g of the styrene oxide product of the formula (38).

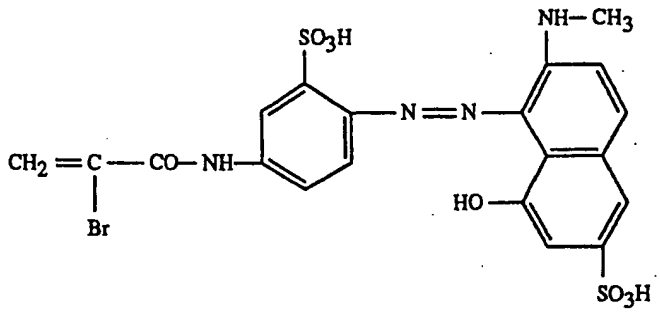
5 g of the dye Acid Black 172 C.I. 15711 are then added. After 10 minutes, the dyeing liquor is heated to 85°C in the course of 45 minutes, and the textile material is maintained at that temperature for 60 minutes with constant circulation. The dyebath is then completely exhausted (dye on the fibre). The textile is then rinsed and dried. A deep and fast black dyeing is obtained on the wool without the conventional heating to the boil. The fastness properties correspond to a dyeing at the boil (98°C).

Similar results are obtained on replacing the styrene oxide product of the formula (38) by the same amount of the bisstyrene oxide product of the formula (50).

Example 8: A circulation dyeing machine is entered with 100 kg of wool packages on a spindle support. In the make-up vessel, 1200 l of water are heated to 60°C. A solution is prepared therein of 1200 g of an aqueous formulation which, based on the formulation, contains

12 % of silicone oil, for example dimethylpolysiloxane,
15 % of 2-ethylhexanol
15 % of paraffin oil
2 % of a water-soluble, surface-active siloxaneoxyalkylene copolymer
8 % of the anionic styrene oxide product of the formula (39) and
2 % of the nonionic styrene oxide product of the formula (38)
and which has been adjusted to pH 8 with monoethanolamine. The liquor is then pumped from the make-up vessel through the material into the dyeing machine and subsequently circulated in alternating direction. Owing to the addition of the product, the dyeing system is spontaneously deaerated and consequently the textile material is thoroughly penetrated.

Thereafter 2 kg of the dye of the formula

(101) 

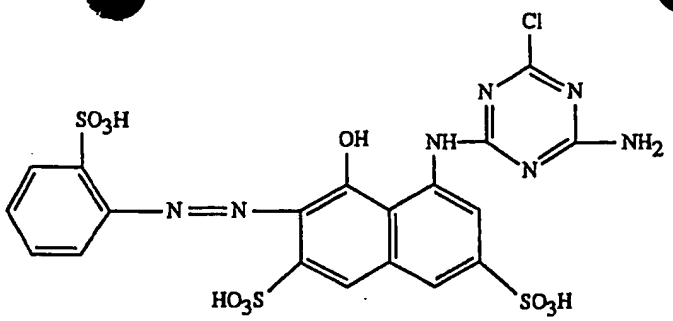
are added to the liquor, followed by 1 kg of a 1:1 mixture of the chloroacetamide-quaternized product of the addition of 7 moles of ethylene oxide to 1 mole of a C_{16}-C_{18}fatty amine mixture and the ammonium salt of the sulfuric acid ester of the product of the addition of 7 moles of ethylene oxide to 1 mole of a C_{16}-C_{18}fatty amine mixture (50 % aqueous preparation), the dyeing liquor is heated to the boil in the course of 30 minutes, and the wool is dyed at the boil for 60 minutes. Virtually no foam develops during dyeing. The result obtained is a strong and uniform dyeing of the package.

The formulation used in this Example is prepared as follows:

12 parts of silicone oil are dissolved in 15 parts of 2-ethylhexanol. 15 parts of paraffin oil, 2 parts of water-soluble, surface-active siloxaneoxyalkylene copolymer, 8 parts of the maleic monoesters of the formula (39), 2 parts of the styrene oxide product of the formula (38), 47.6 parts of water and 0.4 parts of monoethanolamine are then added with continuous stirring, and the mixture is subsequently stirred for a further 30 minutes. The result obtained is a stable formulation having a wetting, deaerating and in particular foam-suppressing effect.

Example 9: In a winch beck, 100 kg of cotton knitwear are wetted out in 3000 l of water containing 3 kg of an aqueous preparation containing, based on the product,
7 % of a silicone oil
11 % of 2-ethylhexanol and
11 % of the anionic styrene oxide product of the formula (41). The cotton is completely wetted and deaerated within 30 seconds. 2 kg of a dye of the formula

(102)



are then added to the liquor together with customary chemicals such as electrolytes and alkalis, and the knitwear is then dyed at the boil for two hours. There are no problems with foaming. The dyed material has a uniform and non-spotty shade.

The preparation used in the Example is prepared as follows:

First, 70 parts of silicone oil are dissolved in 110 parts of 2-ethylhexanol at room temperature. 110 parts of the styrene oxide product of the formula (41) are then added, followed 30 minutes later by 710 parts of water, and thereafter the mixture is stirred for a further 30 minutes. The result obtained is a stable formulation having excellent wetting and deaerating properties.

Example 10: In a short liquor jet, 100 kg of cotton tricot are wetted out in 600 litres of water at 40°C. The liquor is then turned into a dyebath by adding 36 kg of sodium chloride, 5 kg of the dye of the formula (102) and 0.5 kg of a preparation containing

186.75	g of mineral oil (for example Shell Oil L 6189),
185	g of bis-2-ethylhexyl maleate,
10	g of magnesium distearate,
8.25	g of N,N-ethylenebisstearamide,
55	g of a polyoxyethylene derivative of sorbitan tristearate with 20 oxyethylene units, e.g. Tween 65, and
55	g of the anionic styrene oxide product of the formula (13).

The textile material is dyed at 40°C for 45 minutes. 0.6 kg of calcined sodium carbonate is then added, followed after a further 5 minutes by 1.2 kg of aqueous 36 % sodium hydroxide solution. The tricot is then dyed for a further 40 minutes, and then rinsed and washed. The result obtained is a fast, level red dyeing on the tricot. During the dyeing

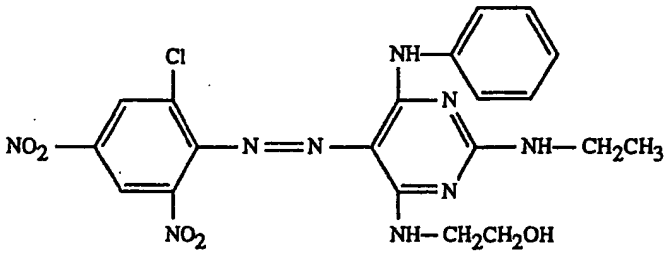
process, there is no foam and there are no problems with the circulation of the textile material.

The preparation used in this Example is prepared as follows:

186.75 g of mineral oil, 185 g of bis-2-ethylhexyl maleate, 10 g of magnesium distearate and 8.25 g of N,N-ethylenebisstearamide are heated with continuous stirring at 110°C until a clear solution is obtained. The solution is cooled down to 45°C in the course of 5 minutes, and 55 g of a polyoxyethylene derivative of sorbitan tristearate with 20 oxyethylene units, e.g. Tween 65, and 55 g of the anionic styrene oxide product of the formula (13) are dispersed therein. The result is a stable formulation which is very effective in particular as an antifoam in alkaline liquors and at high shearing rates.

Example 11: 100 parts of polyester fabric are introduced into a hot dyeing liquor at 60°C containing 1300 parts of water, 2 g/l of ammonium sulfate, 2.5 parts of a dye of the formula

(103)



and 2 parts of an assistant formulation consisting of
16 parts of the anionic styrene oxide product of the formula (39),
24 parts of the product of the addition of 18 moles of ethylene oxide to 1 mole of a C_{12}-C_{18}fatty alcohol mixture and
60 parts of benzyl benzoate

and has been adjusted to pH 5 with formic acid. The liquor temperature is raised to 130°C in the course of 30 minutes and left at that temperature for 60 minutes.

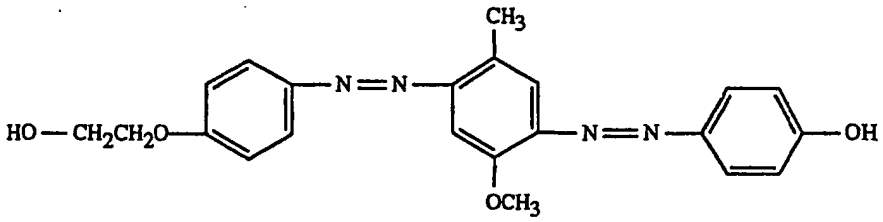
The liquor is then cooled down to 70°C, and dropped, and the polyester fabric is rinsed. Even without the customary reduction clearing a level and rub-fast red dyeing is obtained

with a high colour yield.

The assistant formulation used in this Example is prepared as follows:

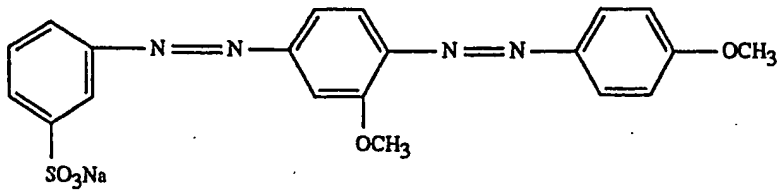
In a heatable stirred vessel, 60 parts of benzyl benzoate are heated to 60°C with continuous stirring, and 24 parts of the product of the addition of 18 moles of ethylene oxide to 1 mole of a C_{12}-C_{18}fatty alcohol mixture and 16 parts of the styrene oxide product of the formula (39) are then stirred in. Cooling down to room temperature leaves a stable formulation which is suitable in particular for dyeing polyester fibres.

Example 12: 100 parts of textured polyester yarns in package form are introduced into an HT dyeing machine which contains 800 parts of hot water, 40°C, 2 parts of ammonium sulfate, 4 parts of a dye of the formula

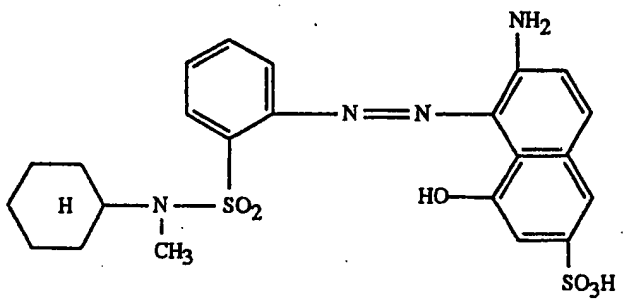
(104) 

and 2 parts of the assistant formulation described in Example 11 and whose liquor has been adjusted to pH 5.5 with formic acid. The temperature of the liquor is then raised to 128°C in the course of 40 minutes, and the textile material is dyed at that temperature for 60 minutes. During the heating-up phase no increase in the differential pressure between the inside and the outside of the yarn package is detectable. Thereafter the liquor is cooled down to 70°C, and the substrate is as usual reduction cleared, rinsed and dried. The result obtained is a strong and level orange dyeing which is notable for good penetration and good fastness properties.

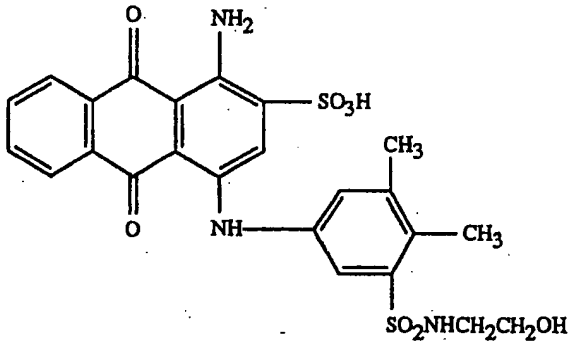
Example 13: A nylon 6.6 loop pile carpet is impregnated on a padder at 25°C with a preparation which contains per litre 1.2 g of a dye of the formula

(105) 

0.8 g of a dye of the formula

(106) 

0.8 g of a dye of the formula

(107) 

5 g of the styrene oxide product of the formula (13) prepared as described in Example 1
2 g of a thickener and
1 g of sodium acetate
and has been adjusted with acetic acid to pH 5-5.5. The liquor pick-up is 320 %. The impregnated carpet is steamed with saturated steam in a dog house steamer at 100°C for 5 minutes. The carpet is then rinsed with cold water and dried. The result obtained is a deep brown dyeing, without frosting, which has the expected fastness properties.

Similar results are obtained on replacing the styrene oxide product of the formula (13) by the same amount of the anionic styrene oxide products of the formulae (32) or (37a) combined with (37b).

Example 14: 100 g of wool serge are wetted out in a circulation machine, for example an Ahiba-turbomat,* at 40°C in the course of 15 minutes with a liquor comprising 1.1 litres of water containing the following additions:

3.2 g of 80 % acetic acid
5 g of calcined sodium sulfate
2 g of an aqueous preparation containing, based on this preparation, 30 % by weight of the styrene oxide product of the formula (38), 10 % by weight of the assistant mixture A_1 described in EP-A-0089004 and
20 % by weight of triethylene glycol monobutyl ether.

4 g of the dye Acid Black 172 C.I. 15711 are then added. After 10 minutes, the dyeing liquor is heated to 90°C in the course of 50 minutes, and the textile material is kept at that temperature with continuous circulation for 60 minutes. The textile material is then rinsed and dried.

The result obtained is a deep, level and fast black dyeing on the wool. The dye bath is 95 % exhausted, although the dyeing was carried out at 90°C. The fastness properties correspond to those of a conventional dyeing at the boil (98°C).

Example 15: The representatives of the styrene oxide products prepared as described in Examples 1 to 5 are tested in wetting power and foam characteristics compared with known products.

A. Wetting power
By test method AL-10-1 using the sink technique

Substrate:	Ladies wool cloth
Amount used:	1 g of active substance per litre

* Trade-mark

B. Foam characteristics:

Foam test by foam plunger method

Apparatus:	Ahiba-Texomat *
Test solution:	200 ml of a 0.1 % aqueous solution of the styrene oxide product
Temperature:	25°C

Number of plunging movements: 60

Assessment of volume of foam: 5 minutes after foam production

C. Surface tension

0.1 g of the styrene oxide product is dissolved in 99.9 g of distilled water. The surface tension (dyn/cm) of the solution is determined with the aid of a tensiometer.

The results in the table below show that the styrene oxide products have better wetting power and foam characteristics than the comparative products.

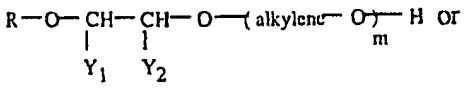
Table

Styrene oxide product of	Wetting (sink time) wool	Foam height (ml)	dyn/cm (mN/m)
Formulae (40a) and (40b)	4"	25	34.3
Formula (27)	2"	0	35.0
Formula (31)	7"	0	33.8
Formula (33)	7"	0	35.4
Formula (35)	4"	20	30.4
Formula (36)	6"	10	30.4
Formula (12)	8"	0	30.9
Ammonium salt of the sulfuric ester of the addition product of 2 mol of ethylene oxide to 1 mol of p-nonylphenol	8"	225	30.1

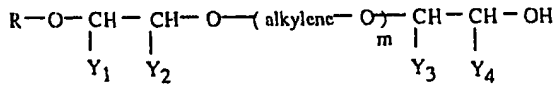
* Trade-mark

WHAT IS CLAIMED IS:

1. A compound of the formula

(1) 

of the formula

(2) 

wherein R is an aliphatic radical having 1 to 24 carbon atoms,
"alkylene" is an alkylene radical of 2 or 3 carbon atoms,
of the substituent pairs (Y_1 and Y_2) and (Y_3 and Y_4) one Y is phenyl and the other Y is hydrogen, and
m is a number from 1 to 100,

its acid ester or a salt thereof.

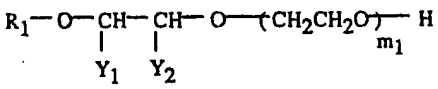
2. A compound according to claim 1, wherein, in the formulae (1) and (2) R is an alkyl or alkenyl radical of 4 to 22 carbon atoms.

3. A compound according to claim 1, wherein, in the formulae (1) and (2) "alkylene" is ethylene.

4. A compound according to claim 1, wherein , in the formulae (1) and (2), m is from 2 to 50.

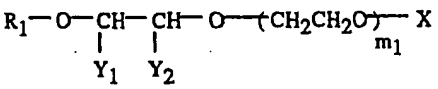
5. A compound according to claim 1, wherein, in the formulae (1) and (2),
m is from 2 to 25.

6. A compound according to claim 1, which is of the formula

(3) 

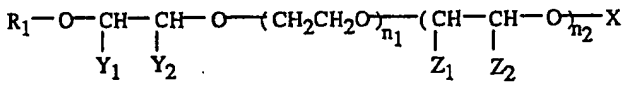
where R_1 is alkyl or alkenyl each having 1 to 22 carbon atoms, one of Y_1 and Y_2 is phenyl and the other is hydrogen, and m_1 is from 2 to 40.

7. An acid ester according to claim 1, which is of the formula

(4) 

where R_1 is alkyl or alkenyl, each having 1 to 22 carbon atoms, one of Y_1 and Y_2 is phenyl and the other is hydrogen, X is the maleic acid, sulfosuccinic acid, sulfuric acid or phosphoric acid radical, and m_1 is 2 to 40.

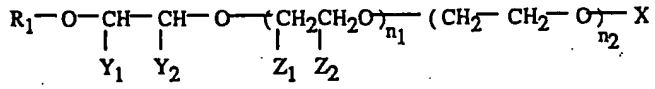
8. An acid ester according to claim 1, which is of the formula

(5) 

where R_1 is alkyl or alkenyl each having 1 to 22 carbon atoms, one of Y_1 and Y_2 is phenyl and the other is hydrogen, one of Z_1 and Z_2 is methyl and the other is hydrogen, X is the maleic acid, sulfosuccinic acid, sulfuric acid or phosphoric acid radical, and

the sum $n_1 + n_2$ is from 2 to 30.

9. An acid ester according to claim 1, which is of the formula

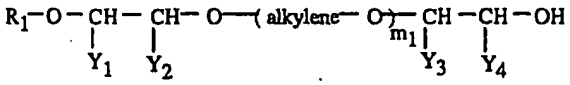
(6) 

where R_1 is alkyl or alkenyl each having 1 to 22 carbon atoms, one of Y_1 and Y_2 is phenyl and the other is hydrogen, one of Z_1 and Z_2 is methyl and the other is hydrogen, X is the

maleic acid, sulfosuccinic acid, sulfuric acid or phosphoric acid radical, and

the sum $n_1 + n_2$ is from 2 to 30.

10. A compound according to claim 1, which conforms to the formula

(7) 

where R_1 is alkyl or alkenyl each having 1 to 22 carbon atoms, "alkylene" is an alkylene radical of 2 or 3 carbon atoms, one of Y_1 and Y_2 is phenyl and the other is hydrogen, m_1 is a number from 2 to 40, and one of Y_3 and Y_4 is phenyl and the other is hydrogen, its acid ester or a salt thereof.

11. A compound according to claim 6 wherein in formula (3) R_1 is 3,5,5-trimethylhexyl and m_1 is 2.

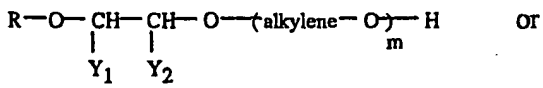
12. A compound according to claim 6 wherein in formula (3) R_1 is dodecyl and m_1 is 2.

13. A compound according to claim 7 wherein in formula (4) R_1 is dodecyl, X is the maleic acid radical and m_1 is 2.

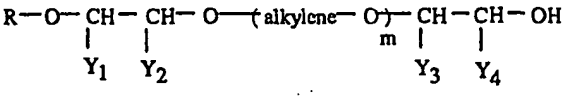
14. A compound according to claim 7 wherein in formula (4) R_1 is dodecyl, X is the sulfuric acid radical and m_1 is 2.

15. A compound according to claim 10 wherein in formula (7) R_1 3,5,5-trimethylhexyl, "alkylene" is ethylene, and m_1 is 10.

16. An aqueous or water-free preparation comprising, based on the preparation as a whole, (A) 2 to 50 % by weight of an acid ester of a compound of the formula

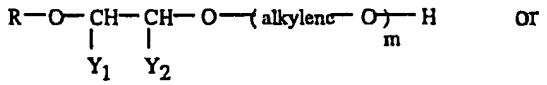
(1)  or

of the formula

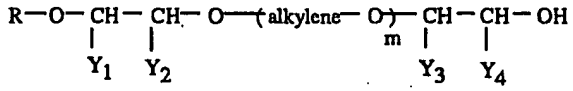
(2) 

where R is an aliphatic radical having 1 to 24 carbon atoms, "alkylene" is an alkylene radical of 2 or 3 carbon atoms, one of Y_1 and Y_2 is phenyl and the other is hydrogen, m is a number from 1 to 100, and one of Y_3 and Y_4 is phenyl and the other is hydrogen,
(B) 5 to 50 % by weight of a nonionic surfactant and at least one of the following components:
(C) 1 to 30 % by weight of a silicone oil,
(D) 10 to 60 % by weight of a mineral oil,
(E) 20 to 45 % by weight of a dialkyl ester of an ethylenically unsaturated aliphatic dicarboxylic acid
(F) 10 to 70 % by weight of an aliphatic or aromatic carboxylic acid ester or an alkylbenzene,
(G) 0.5 to 5 % by weight of a salt of a C_{10}-C_{24}fatty acid and a polyvalent metal and
(H) 0.5 to 3 % by weight of a C_1-C_4alkylenediamide of a fatty acid having 10 to 24 carbon atoms.

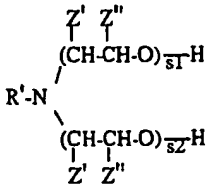
17. An aqueous preparation comprising, based on the preparation as a whole,
(a) 15 to 50 % by weight of a nonionic styrene oxide product of the formula

(1)  or

of the formula

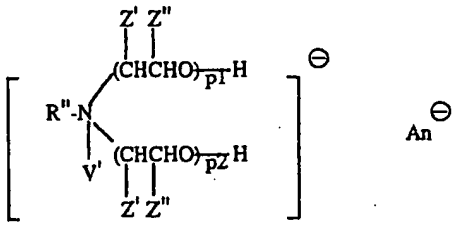
(2) 

where R is an aliphatic radical having 1 to 24 carbon atoms, "alkylene" is an alkylene radical of 2 or 3 carbon atoms, of the substituent pairs (Y_1 and Y_2) and (Y_3 and Y_4) one Y is phenyl and the other Y is hydrogen, and m is a number from 1 to 100,
(b) 1 to 5 % by weight of an acid ester, or salt thereof, of a compound of the formula

(7) 

or of a quaternized product of the acid ester or salt thereof, where R' is alkyl or alkenyl having 12 to 22 carbon atoms, one of Z' and Z" is hydrogen, methyl or phenyl and the other is hydrogen and s_1 and s_2 are each integers such that their sum, $s_1 + s_2$, is from 2 to 100,

(c) 2 to 10 % by weight of a quaternary ammonium compound of the formula

(8) 

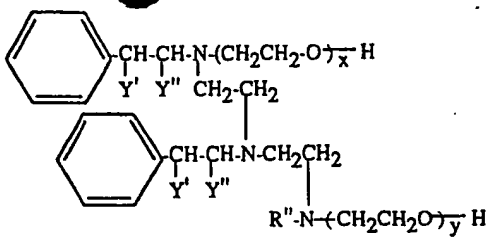
where R" is an alkyl or alkenyl radical having 12 to 22 carbon atoms, V' is substituted or unsubstituted alkyl, one of Z' and Z" is hydrogen, methyl or phenyl and the other is hydrogen, $An^{\ominus}$ is an anion of inorganic or organic acid, and p_1 and p_2 are each integers such that the sum of p_1 and p_2 is from 2 to 100, with or without one or more of the following components:

(d) 0.5 to 25 % by weight of a polyalkylene glycol ether of the formula

(9) 

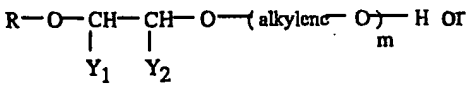
where R''' is an alkyl or alkenyl radical having 4 to 22 carbon atoms, "alkylene" is ethylene or propylene, and q is from 2 to 85, and

(e) 0.5 to 5 % by weight of a nitrogen-containing nonionic compound of the formula

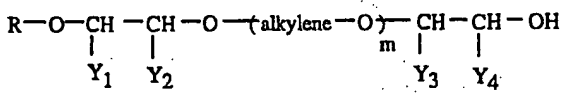
(10) 

where R" is an alkyl or alkenyl radical having 12 to 22 carbon atoms, one of Y' and Y" is phenyl and the other is hydrogen, and x and y are each integers such that the sum of x and y is from 80 to 140.

18. A process for finishing a textile fabric of natural or synthetic fibre material in the presence or absence of appropriate dyes, which comprises finishing in the presence of a nonionic styrene oxide product according to claim 1, of the formula

(1) 

of the formula

(2) 

where R is an aliphatic radical having 1 to 24 carbon atoms,
"alkylene" is an alkylene radical of 2 or 3 carbon atoms,
of the substituent pairs (Y_1 and Y_2) and (Y_3 and Y_4) one Y is phenyl and the other Y is hydrogen, and
m is a number from 1 to 100,
or its anionic acid ester or a salt thereof or a mixture of said nonionic and anionic styrene oxide adducts.

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